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## AN INFRARED AND RAMAN STUDY OF 1,1'-DISUBSTITUTED FERROCENE COMPOUNDS

J. N. WILLIS, JR., M. T. RYAN,  
F. L. HEDBERG, and H. ROSENBERG

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# **AN INFRARED AND RAMAN STUDY OF 1,1'-DISUBSTITUTED FERROCENE COMPOUNDS**

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## FOREWORD

This report was prepared by the Analytical Branch, Materials Physics Division, Air Force Materials Laboratory. The work was initiated under Project No. 7367, "Experimental Techniques for Materials Research," Task No. 736702, "Physical-Chemical Methods for Materials Analysis," and administered by the Air Force Materials Laboratory, Directorate of Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Lt. J. N. Willis, Jr., Project Engineer in conjunction with the Nonmetallics Division, Polymer Branch, (Dr. H. Rosenberg and Dr. F. L. Hedberg).

This report covers work performed from June 1966 to July 1967. The manuscript was released by the authors in July 1967 for publication.

This technical report has been reviewed and is approved.



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## ABSTRACT

The infrared ( $4000-55\text{ cm}^{-1}$ ) and Raman ( $3200-75\text{ cm}^{-1}$ ) spectra of 1,1'-dibromo-, 1,1'-diiodo-, and 1,1'-dichloroferrocene are reported. An attempt is made to give a complete vibrational assignment for all fundamental vibrations of these molecules. The results of these assignments are compared to those of 1,1'-dimethylferrocene (Reference 2) and of monosubstituted benzenes (References 3, 10). The assigned frequencies were tested by utilizing the inequality rule of Whiffen and Steele.

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## SECTION I

### INTRODUCTION

The aromatic nature of metal cyclopentadienyl compounds has been a subject of discussion in the literature over the past several years. Lippincott and Nelson (Reference 1) have assigned the vibrational spectra of ferrocene and ruthenocene and compared the aromatic nature of ferrocene with benzene and tropylium ion. Bailey and Lippincott (Reference 2) have assigned the vibrational spectrum of 1,1'-dimethylferrocene and have compared the changes between the ferrocene-dimethylferrocene spectra with the benzene-toluene spectral changes.

The recent development of laser excitation has made accessible the previously difficult-to-obtain Raman spectra of colored ferrocene compounds. Also, the 1,1'-dichloro-, dibromo-, and diiodoferrocenes have recently been synthesized as part of a research program in this laboratory to develop ferrocene polymers. We have recorded the infrared and Raman spectra of these compounds and report here the vibrational assignment of the observed frequencies. A comparison of these assignments with the work of Whiffen (Reference 3) on the vibrational spectra of halobenzenes as well as the Bailey and Lippincott assignment of 1,1'-dimethylferrocene has provided some additional information on the aromatic nature of the cyclopentadienyl ring in ferrocene.

## SECTION II

### INFRARED SPECTRA

The infrared spectra were obtained over the range  $55\text{--}4000\text{ cm}^{-1}$ . The  $55\text{--}350\text{ cm}^{-1}$  region was investigated using the Perkin-Elmer model 301 grating spectrophotometer. The  $250\text{--}4000\text{ cm}^{-1}$  region was investigated using Perkin-Elmer model 521 and model 225 grating spectrophotometers. Atmospheric water vapor was removed from the various instruments by flushing with dry nitrogen. In the higher wavenumber region, the instruments were calibrated in the usual manner (Reference 4). The lower region was calibrated using atmospheric water vapor (Reference 5).

Liquid cells with CsI plates and various spacers were used to obtain the spectra of the three compounds in approximately 10% solutions of carbon disulfide and carbon tetrachloride. Infrared spectra were also recorded on liquid films of the three compounds using CsI plates. The spectra of the liquid films were almost identical to those observed for the solutions. Certain exceptions to this will be discussed later. To obtain liquid films of the 1,1'-dichloro- and dibromoferrocenes, it was necessary to use a small coil of nichrome wire heated by means of a Variac to just above the melting points of the compounds. The spectra of solid 1,1'-dichloroferrocene was obtained by heating the compound as discussed above and slowly lowering the temperature until the compound crystallized.

The spectra of all the compounds as saturated and dilute solutions in cyclohexane were recorded from 350 to 55  $\text{cm}^{-1}$ . Liquid cells with polyethylene windows and a path length of about 1.0 mm were used in this region. The far infrared spectra of solid 1,1'-dibromoferrocene was obtained using 20 mg of sample in a matrix of 200 mg of low density polyethylene.

The frequency measurements reported for the region 4000-250  $\text{cm}^{-1}$  were made from the expanded scale spectra of the liquid films and solutions. Figures 1 to 3 show typical infrared spectra of liquid films of the three samples from 4000-200  $\text{cm}^{-1}$ . Figures 4 to 5 show the infrared spectra from 350 to 55  $\text{cm}^{-1}$  of 1,1'-dibromo- and diiodoferrocene. Due to the limited amount of 1,1'-dichloroferrocene available, the far infrared spectrum was very poor. For this reason, it is not included. The measured frequencies are listed in Tables Ia, Ib, and Ic. These frequencies are believed to be accurate to  $\pm 2 \text{ cm}^{-1}$  for the sharp bands and  $\pm 4 \text{ cm}^{-1}$  for the weak bands.

### SECTION III

#### RAMAN SPECTRA

The Raman spectra of the 1,1'-dichloro-, 1,1'-dibromo-, and 1,1'-diiodoferrocenes were investigated using a Perkin-Elmer model LR-1 spectrometer equipped with a Spectra Physics Model 125 helium-neon laser. All spectra were observed using 6328<sup>0</sup>A excitation with an estimated intensity of 50 mw. The spectra for 1,1'-dibromo- and 1,1'-diiodoferrocene were obtained in saturated solutions of benzene or carbon tetrachloride using a 0.2 ml multipass quartz cell. The spectra obtained from 1,1'-dichloroferrocene were taken using a small single crystal. Quite drastic changes were noted in certain bands in the spectrum when the crystal was rotated (Figure 6). All quoted frequencies were obtained with the Raman energy passing along the "A" axis. This sample was less pure than used for the infrared spectra. Since the Raman data for 1,1'-dibromo- and 1,1'-diiodoferrocene were obtained from solutions and the 1,1'-dichloroferrocene frequencies were taken from a single crystal, some shifts in frequency position are expected. The frequencies are expected to be accurate to  $\pm 2 \text{ cm}^{-1}$  for the strong bands and  $\pm 4 \text{ cm}^{-1}$  for the weak or broad bands.

## SECTION IV

### EXPERIMENTAL

1,1'-dichloroferrocene was prepared by a modification of the method of Nefedov and Nefedova (Reference 6) from 1,1'-bis(chloromercuri)ferrocene and cupric chloride with aqueous tetrahydrofuran as solvent in 18% yield. Purification by preparative vapor phase chromatography (V.P.C) afforded crystals with melting point 80° to 81°C of 99+% purity by V.P.C. analysis.

1,1'-dibromoferrocene was prepared by the method of Nesmeyanov et al (Reference 7) from ferrocenyl-1,1'-diboronic acid and cupric bromide. Purification by crystallization from hexane afforded material of melting point 54° to 56°C which was found to be 99% pure by V.P.C. analysis.

1,1'-diiodoferrocene was prepared by a modification of the method of Fish and Rosenblum (Reference 8) from 1,1'-bis(chloromercuri)ferrocene and 1,3-diiodo-5, 5-dimethylhydantoin with tetrahydrofuran as solvent in 50% yield. Purification by preparative V.P.C. afforded liquid 1,1'-diiodoferrocene of 99% purity by V.P.C. analysis. 1,1'-diiodoferrocene was found to degrade in the presence of copper or iron at elevated temperature (>170°C). This made it necessary to use an all glass-Teflon V.P.C. column. The column which was 3/8-in. O.D. and 1.5 ft in length, was packed with 10% Apiezon L on firebrick. Samples were injected directly onto the column which was held at 160°C. The purity of the 1,1'-diiodoferrocene was found to be 99% by V.P.C analysis.

When the purity of the 1,1'-disubstituted ferrocenes was very high (99.9%), there was a complete absence of the  $1105\text{ cm}^{-1}$  band. The presence of this band in several of the compounds thought to be very pure led us to further check on the sample. Mass spectral data revealed that the impurity was a 1,2- or a 1,3-dihalogenated ferrocene. Thus far, we have been unable to remove this impurity from the samples in use.

## SECTION V

### INTERPRETATION

It is a good assumption that there is no interaction between rings of the disubstituted compound. Thus it becomes possible to interpret the ring modes of these compounds in terms of only one substituted ring. An isolated monosubstituted cyclopentadienyl ring where the substituent is considered a point group has  $C_{2v}$  symmetry. This would allow twenty-four fundamental modes ( $8a_1 + 7b_1 + 3a_2 + 3b_2$ ) and three C-X modes ( $a_1 + b_1 + b_2$ ). The assignment of these fundamentals is aided if one compares them to similar modes found in A the cyclopentadienyl rings of ferrocene and B the monosubstituted benzenes.

The compounds of primary interest in this study were 1,1'-dichloro-, 1,1'-dibromo-, and 1,1'-diiodoferrocene. All reference to 1,1'-disubstituted ferrocene compounds shall simply be referred to as "disubstituted". However, the spectra of two other 1,1'-disubstituted ferrocenes were also found to be helpful in this study. The compounds were 1,1'-dimethylferrocene and 1,1'-ferrocenedialdehyde. The dimethyl compound has been studied by Bailey and Lippincott (Reference 2) and the Raman frequencies quoted here are taken from that work. The approximate description of the fundamental vibrations is to be discussed by class.

#### CLASS $a_1$

Two  $a_1$  and two  $b_1$  C-H stretching modes are expected. The highest C-H stretching mode in ferrocene was found at  $3099\text{ cm}^{-1}$ . This should give rise to an  $a_1$  C-H stretching mode in the disubstituted compounds. The band found at 3110, 3105, and  $3100\text{ cm}^{-1}$  is assigned to this mode. The degenerate C-H stretching modes observed in ferrocene at  $3085\text{ cm}^{-1}$  should give rise to one  $a_1$  and two  $b_1$  C-H stretching modes. These are assigned to the bands at 3090, 3085, and  $3080\text{ cm}^{-1}$  in the disubstituted haloferrocenes. There should be two  $a_1$  and two  $b_1$  C-C stretches in the substituted ferrocenes. These four modes arise from the ferrocene C-C stretching modes assigned to the band at  $1560\text{ cm}^{-1}$  and the bands at  $1408\text{-}1411\text{ cm}^{-1}$  (Reference 1). The two  $a_1$  modes in the substituted compounds would be expected to appear as strong bands in the Raman spectrum. The Raman spectrum of dibromoferrocene shows four bands between  $1350\text{ and }1410\text{ cm}^{-1}$ , the two higher frequency bands being of greater intensity than the lower frequency bands. The Raman spectrum of diiodoferrocene shows two bands of medium intensity at 1404 and  $1371\text{ cm}^{-1}$ . The Raman spectrum of dichloroferrocene also has two bands in this region at 1416 and  $1384\text{ cm}^{-1}$ . No consistent infrared bands between  $1450\text{ and }1600\text{ cm}^{-1}$  are observed for the dihalo compounds studied. However, a series of strong bands are found at lower frequencies between  $1320\text{ and }1420\text{ cm}^{-1}$ . These observations led to the consideration of reassigning the C-C stretching modes in ferrocene.

In support of this, several facts are presented:

1. The only reason used in assigning the  $E_{2u} - E_{2g}$  C-C stretching modes in ferrocene to the weak band at  $1560\text{ cm}^{-1}$  was the analogy to the similar mode in benzene. This band was not found in the spectra of ruthenocene or nickelocene (Reference 2).

2. There are weak bands in the Raman spectra of ferrocene and ruthenocene at  $1356\text{ cm}^{-1}$  and  $1360\text{ cm}^{-1}$  which could be assigned to these modes (Reference 1). This band was described as a combination band of  $\omega_4 + \omega_{25}$  by Lippincott and Nelson. This combination predicts a band at  $1353\text{ cm}^{-1}$  in ferrocene and at  $1386\text{ cm}^{-1}$  in ruthenocene. The disagreement between calculated and observed values for this assignment in ruthenocene is clearly so large as to be suspect.

3. There is a similar band found in the Raman spectrum of cyclopentadienyl-Manganese tricarbonyl at  $1365\text{ cm}^{-1}$  (Reference 9). However, no band is found in the Raman spectrum of this compound around  $1560\text{ cm}^{-1}$ .

4. As stated above, a series of bands is found in the spectra of the dihalo compounds between  $1410$  and  $1326\text{ cm}^{-1}$  (Table I). The Raman and infrared spectra indicate the presence of four fundamentals in this region.

This evidence has persuaded us to reassign the  $E_{2g} - E_{2u}$  modes in ferrocene to  $1356\text{ cm}^{-1}$  which is below the  $E_{1g} - E_{1u}$  modes at  $1408$  and  $1411\text{ cm}^{-1}$ . It follows that the highest  $a_1$  mode in the dihalo series is assigned to the band at  $1417$ ,  $1410$ , and  $1402\text{ cm}^{-1}$ . The other  $a_1$  mode is assigned to the band at  $1385$ ,  $1380$ , and  $1378\text{ cm}^{-1}$ , respectively. The two  $b_1$  modes are assigned to the series  $1360$ ,  $1355$ , and  $1345\text{ cm}^{-1}$  and  $1349$ ,  $1342$ , and  $1326\text{ cm}^{-1}$ . To further this argument, a close study of analogous benzene modes was made. In the chloro-, bromo-, and iodobenzene series, four C-C stretching modes are observed. The two highest modes are observed around  $1600\text{ cm}^{-1}$  as a strong band with an associated shoulder. In the case of benzaldehyde, the adjacent carbonyl group splits the two high frequency modes into bands of medium intensity. In 1,1'-ferrocenedialdehyde, the same splitting and enhancement of intensity is observed but not in the case of two lower modes ( $1370$  and  $1332\text{ cm}^{-1}$ ).

The next  $a_1$  mode closely resembles the vibration Whiffen calls "q" in monosubstituted benzene (Reference 3). In toluene (Reference 10) and in the halobenzenes (Reference 3), the bands Whiffen describes as "q" and "r" are found to interact to a considerable extent. These bands are  $a_1$  modes and are X-sensitive. They arise from (A) the ring breathing and (B) C-X stretching modes. Since both of these modes involve considerable C-X stretching, they can no longer be adequately described as (A) or (B). They are better described as X-sensitive  $a_1$  modes. The same phenomenon is found in substituted ferrocenes. The highest mass-sensitive band in the substituted ferrocenes is found at  $1170$ ,  $1152$ , and  $1142\text{ cm}^{-1}$  for

the halogen series and at  $1229\text{ cm}^{-1}$  in dimethylferrocene (Reference 2). The next X-sensitive band of sufficient intensity in the infrared and Raman to be assigned to an  $a_1$  fundamental is found at 884, 872, and  $865\text{ cm}^{-1}$  in the halogen series. Lippincott and Bailey assigned this mode to the band at  $1021\text{ cm}^{-1}$  in dimethylferrocene. The  $1020\text{ cm}^{-1}$  band was found to be non-X-sensitive in the halogen series. The more likely choice for this assignment in dimethylferrocene is the band at  $919\text{ cm}^{-1}$ .

The two  $a_1$  C-H in-plane deformations which arise from the ferrocene modes at 1178 and  $1002\text{ cm}^{-1}$  are expected close to these frequencies. The highest  $a_1$  C-H deformation is assigned to the bands at 1178, 1178, and  $1175\text{ cm}^{-1}$  in the halogen series due to their strength in the infrared and Raman spectra. The other  $a_1$  mode is assigned to the strong band observed at  $1020\text{ cm}^{-1}$  in the compounds studied. This leaves but one  $a_1$  vibration. This mode arises from an  $E_{2g}$  ring distortion predicted to be at  $880\text{ cm}^{-1}$  in ferrocene. There are three choices for this mode: a series of weak bands at  $850\text{ cm}^{-1}$ , a series of strong bands around  $820\text{ cm}^{-1}$ , or a series of strong-to-medium bands around  $805\text{ cm}^{-1}$ . The band found around  $820\text{ cm}^{-1}$  is best assigned to a  $b_2$  C-H deformation due to its strength in the infrared. The Raman spectrum of diiodoferrocene and dichloroferrocene have bands at 847 and  $833\text{ cm}^{-1}$ , respectively, but no bands around  $800\text{ cm}^{-1}$ . The  $a_1$  ring distortion is assigned to the bands around  $850\text{ cm}^{-1}$  for the dihalo series. This agrees with the assignment in the case of dimethylferrocene. The  $805\text{ cm}^{-1}$  series are best assigned to an  $a_2$  C-H deformation. This band is found to be rather strong in the compounds studied. This vibration in dimethylferrocene was assigned to a band at  $833\text{ cm}^{-1}$  which is also rather strong. It is unusual to find an  $a_2$  fundamental so strong in the infrared spectrum. However, the appearance of this band is essentially unchanged from that in ferrocene where it appears as a shoulder on the strong  $811\text{ cm}^{-1}$  band. The Steele and Whiffen inequality rule (Reference 11) was a great aid in this assignment (see Results for an explanation of this rule).

#### CLASS $b_1$

Four  $b_1$  modes have already been discussed. Of the remaining four modes, the highest arises from the  $A_{2g}$  C-H deformation in ferrocene which is predicted to be at  $1200\text{ cm}^{-1}$ . A weak band is observed at about  $1205\text{ cm}^{-1}$  in all compounds studied which is assigned to the expected C-H deformation. The  $b_1$  C-H deformation mode arising from the  $1178\text{ cm}^{-1}$  mode in ferrocene is assigned to the bands found at  $1153\text{ cm}^{-1}$  in the halogen series. The next mode arises from the  $1010\text{ cm}^{-1}$  band in ferrocene. This mode is only directly observed in the spectrum of dibromoferrocene at  $878\text{ cm}^{-1}$ . The corresponding band in dichloroferrocene is probably hidden by the strong band at  $884\text{ cm}^{-1}$ . A band is observed at  $883\text{ cm}^{-1}$  in the spectrum of the liquid film of diiodoferrocene which is probably the same vibration shifted somewhat due to the change in phase. This leaves one  $b_1$  fundamental, an X-sensitive

mode which approximates a C-X in-plane bending. This arises from a C-H deformation found in ferrocene at  $1010\text{ cm}^{-1}$ . The corresponding benzene frequencies are found at 297, 254, and  $200\text{ cm}^{-1}$  (Reference 3). The band in the substituted ferrocenes is found at 251, 237, and  $202\text{ cm}^{-1}$ .

#### CLASS $b_2$

The highest mode in this class arises from a C-H deformation at  $1050\text{ cm}^{-1}$  in ferrocene. This mode is assigned to the strong bands between 1014 and  $1010\text{ cm}^{-1}$  in this series. The ring deformation mode in ferrocene predicted to be at  $500\text{ cm}^{-1}$  should give rise to a  $b_2$  X-sensitive mode. In the substituted halobenzenes, this mode is assigned to bands at 457, 460, and  $450\text{ cm}^{-1}$ . Lippincott and Bailey assign this mode at  $632\text{ cm}^{-1}$  in dimethyl ferrocene. There are weak bands at 430, 421, and  $402\text{ cm}^{-1}$  in the dihaloferrocene series which could be assigned to this mode. However, these are weak infrared bands and appear to be rather low in frequency for this assignment. This mode may be obscured by the intense bands associated with the ring-metal modes discussed below. The lowest  $b_2$  mode is an X-sensitive mode approximately described as an out-of-plane C-X deformation. The corresponding bands for the chloro-, bromo-, and iodobenzene are found at 196, 181, and  $166\text{ cm}^{-1}$ . This mode is assigned to the band at 225 in dichloro-, 206 in dibromo-, and  $180\text{ cm}^{-1}$  in diiodoferrocene. The bands in dichloro- and dibromo- derivatives were only observed in the spectrum of the solid.

#### CLASS $a_2$

Although these bands are forbidden in the infrared spectrum, they are quite often observed in the spectrum of the liquid and solid. The mode occurring at the highest frequency is a C-H deformation arising from the  $1050\text{ cm}^{-1}$  band in ferrocene. Weak bands found around  $1050\text{ cm}^{-1}$  are assigned to this mode. The second  $a_2$  vibration arises from the  $834\text{ cm}^{-1}$  ring distortion in ferrocene and has already been discussed. The last  $a_2$  mode is a ring deformation arising from the band in ferrocene estimated to be at  $500\text{ cm}^{-1}$ . The mode is assigned to weak bands at 605, 599, and  $592\text{ cm}^{-1}$ . This seems to indicate that the original estimate of  $500\text{ cm}^{-1}$  for ferrocene is too low in this case.

## SECTION VI

### RING-METAL VIBRATIONS

The assignment of the ring-metal modes is aided by comparison with ferrocene. The "sandwich" compounds should have five infrared and Raman active modes; a symmetric and antisymmetric stretch, a symmetric and antisymmetric tilt and a bend. In this series of molecules, the possibility of more than one isomer exists. If the molecule existed in the trans form, the symmetry would be  $C_{2h}$ . This would preclude coincidences between infrared and Raman frequencies due to the ring-metal modes. The other isomers, two gauche forms and a cis form are of lower symmetry and selection rules allow coincidences for the ring-metal mode. Since coincidences are observed, one can assume that the molecules do not exist solely in the trans form. This evidence does not allow one to conclude that any one of the isomers is the predominant form.

The tilting modes are degenerate in ferrocene and the reduction in symmetry in the substituted compounds should split these modes. The symmetric ring tilt is found at  $388\text{ cm}^{-1}$  in ferrocene. This mode is assigned to the bands at 390, 327-323, and  $283\text{--}272\text{ cm}^{-1}$ . The expected splitting is observed only in the dibromo- and diiodoferrocene. By analogy to ferrocene, the R-M antisymmetric tilt is assigned to 513, 498, and  $490\text{ cm}^{-1}$ . The expected splitting was not observed in this mode.

The R-M antisymmetric stretch is found at 491, 488, and  $483\text{ cm}^{-1}$ . In diiodoferrocene run as a film of the pure liquid the antisymmetric tilt and stretch appear as a broad band at  $490\text{ cm}^{-1}$ . In  $\text{CS}_2$  solution, splitting of these modes is observed. The symmetric ring-metal stretch is found at  $303\text{ cm}^{-1}$  in ferrocene. The corresponding bands in the substituted compounds are expected to be very strong in the Raman spectra. Dichloro-, dibromo-, and diiodoferrocene have very strong bands in the Raman spectra at 344, 343, and  $326\text{ cm}^{-1}$  which are assigned to this mode. The "low" frequency in the case of dichloroferrocene may be due to the different states from which the frequencies were obtained.

The last mode to be assigned is the ring-metal-ring bending. This mode was observed in our laboratory at  $170\text{ cm}^{-1}$  in ferrocene (in cyclohexane solution). A band is found at  $171\text{ cm}^{-1}$  in all of the dihalo compounds and is assigned to this mode.



## SECTION VII

## RESULTS

During this investigation, several bands in the infrared spectra were found to be phase sensitive. This was particularly obvious in the case of the ring-metal vibrations. The antisymmetric ring tilting vibration of dichloroferrocene was found at  $513\text{ cm}^{-1}$  in solution,  $502\text{ cm}^{-1}$  in the melt, and split into two bands at  $500$  and  $510\text{ cm}^{-1}$  in the solid. This band is observed at  $504\text{ cm}^{-1}$  in dibromoferrocene and at  $490\text{ cm}^{-1}$  in diiodoferrocene in  $\text{CS}_2$  solution. The symmetric ring-metal tilting and antisymmetric ring-metal stretching were also found to follow this pattern of shifting with changes in phase. The symmetric ring-metal stretching was not observed in dichloroferrocene, but in dibromoferrocene it also appears to shift with changes in phase.

A comparison of the solution spectra of the dihaloferrocenes indicates that all of the ring-metal vibrations shift to lower frequency from dichloro- to dibromo- to diiodoferrocene with the exception of the ring-metal-ring bending which was found at  $171\text{ cm}^{-1}$  in all the compounds studied. The symmetric and antisymmetric ring tilting vibrations show a linear dependence on the square root of the reduced mass of  $\text{Fe-C}_5\text{H}_4\text{-X}$ , where X is the halogen (Figure 7). The antisymmetric and symmetric ring-metal stretching vibrations vary linearly as the electronegativity of the halogen (Figure 8).

As a result of this investigation and other studies, previous conclusions concerning the force constants of ferrocene seem to be questionable. A recent electron diffraction study of ferrocene (Reference 12) indicated that the C-H bonds in ferrocene are bent  $5^\circ$  out of the plane of the carbon ring towards the metal atom. The C-C bond length of  $1.431\text{ \AA}$  calculated from the electron diffraction study is somewhat longer than the C-C bond length in benzene ( $1.39\text{ \AA}$ ). A study of the cyclopentadienide anion by Sado et al (Reference 13) reports lower frequencies in the  $\text{C}_5\text{H}_5$  ring for two of the C-C stretching modes than assigned in the  $\text{C}_5\text{H}_5$  ring in ferrocene by Lippincott and Nelson (Reference 1). The anion has  $D_{5h}$  symmetry and the  $A_1'$ ,  $E_1'$ , and  $E_2'$  C-C stretches were assigned at  $983$ ,  $1455$ , and  $1447\text{ cm}^{-1}$ , respectively. The comparable frequencies from the work of Lippincott and Nelson are  $1105$ ,  $1411$ , and  $1560\text{ cm}^{-1}$ , respectively. Yet normal coordinate analyses based on these widely different assignments for a  $\text{C}_5\text{H}_5$  ring both yield force constants which indicate an aromatic C-C linkage. Our results on the dihaloferrocenes indicate agreement with the  $1105$  and  $1411\text{ cm}^{-1}$  assignments but show a much lower frequency for the third C-C stretching mode. These facts indicate that a reexamination of the force constants for bonds in ferrocene is needed.

Since it is virtually impossible to get good vapor spectra of these compounds and at present no Raman polarization data are available, other means of checking the assignments

are needed. One method which has proven useful in other similar studies has been the use of the inequality rule of Steele and Whiffen (Reference 11). This rule states that any frequency,  $\nu_j$ , of the lighter molecule has to be higher in frequency than the  $\nu_{j+1}$  frequency of the heavier molecule. This, combined with the normal rule that for similar vibrations the  $\nu_j$  frequency of the heavier molecule cannot be higher than the  $\nu_j$  frequency of the lighter molecule, means that frequency ranges can be given for each vibration. The use of the inequality rule is shown in Table IV.

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TABLE I

## OBSERVED VIBRATIONAL SPECTRA OF 1,1'-DICHLOROFERROCENE ++

Infrared	Raman	Assigned
3110 w		$a_1 \nu \text{ C-H}$
3090 w		$a_1 \nu \text{ C-H} + b_1 \text{ CH}$
2210 w		?
1755 w		$884 + 884 = 1768 \text{ cm}^{-1}$
1725 w		$884 + 851 = 1725 \text{ cm}^{-1}$
1675 vw*		$851 + 819 = 1670 \text{ cm}^{-1}$
1650 vw*		$820 \times 2 = 1640 \text{ cm}^{-1}$
1560 vvw*		$1385 + 171 = 1556 \text{ cm}^{-1}$
1473 vw*		$884 + 605 = 1489 \text{ cm}^{-1}$
1417 vs	1416 w	$a_1 \nu \text{ C-C}$
1385 w-m	1384	$a_1 \nu \text{ C-C}$
1360 m		$b_1 \nu \text{ C-C}$
1349 sh		$b_1 \nu \text{ C-C}$
1258 w		$1014 + 251 = 1265 \text{ cm}^{-1}$
1205 w		$b_1 \delta \text{ C-H}$
1178 m		$a_1 \delta \text{ C-H}$
1170 s	1172 s	$a_1 \text{ X-sensitive}$
1153 w		$b_1 \delta \text{ C-H}$
1106 m	1111 vw	impurity
1050 w	1070 w	$a_2 \delta \text{ C-H}$
1022 s	1032 m	$a_1 \delta \text{ C-H}$
1014 m		$b_2 \delta \text{ C-H}$
1000 w-sh		impurity
900 sh		?
884 s	884 w	$a_1 \text{ X-sensitive and}$ $b_1 \text{ ring distortion}$

TABLE I (CONTD)

Infrared	Raman	Assigned
851 w	833 w	$a_1$ ring distortion
819 s		$b_2$ $\delta$ C-H
805 s		$a_2$ $\delta$ C-H
605 w	594 w	$a_2$ $\delta$ ring
513 s	507 vw	antisymmetric R-M tilting
491 s		antisymmetric R-M stretching
430 w*	422 w	$b_2$ $\delta$ ring ?
390 w	494 w-m	symmetric R-M tilting
	344 vs	symmetric R-M stretching
251 w**	252 s	$b_1$ X-sensitive
225 w**	- - - -	$b_2$ X-sensitive
171 w**	- - - -	R-M-R bending
† Frequencies are in reciprocal centimeters		
+ v(very), s(strong), m(medium), w(weak), br(broad), sh(shoulder)		
* obtained from liquid film		
** obtained from solid		

TABLE II

## OBSERVED VIBRATIONAL SPECTRA OF 1,1'-DIBROMOFERROCENE † †

Infrared	Raman	Assignment
3105 m	3110 w	$a_1$ v C-H
3085 w		$a_1 + b_1$ C-H
1759 m		$872 + 878 = 1750$
1727 m		$872 + 850 = 1722$
1700 w		$872 + 820 = 1692$
1670 w		$850 + 820 = 1670$
1645 w		$820 \times 2 = 1640$
1630 w*		$820 + 809 = 1629$
1545 vw*		$1380 + 171 = 1551$
1473 w*		$878 + 599 = 1477$
1410 vs	1410 m	$a_1$ v C-C
1380 m	1381 w-m	$a_1$ v C-C
1355 m-s	1363 w**	$b_1$ v C-C
1350 w-sh		$1178 + 171 = 1349$
1342 w	1352 w**	$b_1$ v C-C
1202 w	1203 m	$b_1$ $\delta$ C-H
1178 m	1179 sh	$a_1$ $\delta$ C-H
1152 vs	1154 vs	$a_1$ X-sensitive + $b_1$ C-H
1106 w	1106 vw	impurity
1050 m	1059 m	$a_2$ $\delta$ C-H
1020 s	1021 s	$a_1$ $\delta$ C-H
1010 m-s		$b_2$ $\delta$ C-H
930 w		$599 + 339 = 938$
878 sh		$b_1$ ring distortion
872 vs	876 s	$a_1$ X-sensitive

TABLE II (CONTD)

Infrared	Raman	Assignment
850 w		$a_1$ ring distortion
820 s		$b_2$ $\delta$ C-H
809 m		$a_2$ $\delta$ C-H
612 vw		$419 + 206 = 625$
599 w	591 w	$a_2$ $\delta$ ring
498 vs		antisym. R-M tilting
488 vs-br	491 vw	antisym. R-M stretching
	456 w	$237 \times 2 = 464$
419 m-br	410 br	$b_2$ $\delta$ ring ?
339 w**	343 m	sym. R-M stretching
327 m } 323 m } split	305 w	sym. R-M tilting
262 vw		
237 w	225 w	$b_1$ X-sensitive
206 w**		$b_2$ X-sensitive
171 w		R-M-R bending
† Frequencies are in reciprocal centimeters		
+ v(very), s(strong), m(medium), w(weak), br(broad), sh(shoulder)		
* obtained from liquid film		
** obtained from solid		

TABLE III

## OBSERVED VIBRATIONAL SPECTRA OF 1,1'-DIIDOFERROCENE ++

Infrared	Raman	Assignment
3100 m	3110 w	$a_1 \nu \text{ C-H}$
3080 w		$a_1 \nu \text{ C-H} + b_1 \nu \text{ C-H}$
1760 m		$865 + 883 = 1648$
1730 m		$883 + 848 = 1731$
1712 w		$865 + = 1713$
1670 m*		$820 + 848 = 1668$
1635 m*		$820 \times 2 = 1640$
1537 vw*		$1378 + 171 = 1549$
1422 vw		$1020 + 398 = 1418$
1402 s	1404 m	$a_1 \nu \text{ C-C}$
1378 s	1371 m	$a_1 \nu \text{ C-C}$
1345 s		$b_1 \nu \text{ C-C}$
1326 sh		$b_1 \nu \text{ C-C}$
1290 vw		$1020 + 275 = 1295$
1200 w		$b_1 \delta \text{ C-H}$
1175 w-m	1178 w	$a_1 \delta \text{ C-H}$
1150 sh		$b_1 \delta \text{ C-H}$
1142 s	1168 m	$a_1 \text{ X-sensitive}$
1050 m	1060 w	$a_2 \delta \text{ C-H}$
1020 vs	1017 m	$a_1 \delta \text{ C-H}$
1010 s		$b_2 \delta \text{ C-H}$
925 w		$592 + 326 = 918$
910 sh		?
883 sh*		$b_1 \text{ ring distortion}$
865 vs	864 s	$a_1 \text{ X-sensitive}$



TABLE III (CONTD)

Infrared	Raman	Assignment
848 m	847 w	$a_1$ $\delta$ ring
820 s		$b_2$ $\delta$ C-H
805 m		$a_2$ $\delta$ C-H
760 w*		$483 + 275 = 758$
592 w*	587 w	$a_2$ $\delta$ ring
490 vs	487 s	antisym. R-M tilting
483 vs-br		antisym. R-M stretching
398 m*	401 w-m	$b_2$ $\delta$ ring ?
323 w	326 s	sym. R-M stretching
283 m } split 272 m }	273 m	sym. R-M tilting
213 m	198 w	$b_1$ X-sensitive
202 m		?
180 m		$b_2$ X-sensitive
171 m		R-M-R bending
	78 w	$273 - 198 = 75$
† Frequencies are in reciprocal centimeters		
+ v(very), s(strong), m(medium), w(weak), br(broad), sh(shoulder)		
* obtained from liquid film		

TABLE IV  
ASSIGNED FREQUENCIES UTILIZING  
THE STEELE AND WHIFFEN INEQUALITY RULE

Ferrocene	1,1'-Dichloroferrocene	1,1'-Dibromoferrocene	1,1'-Diiodoferrocene
		<u>Class a<sub>1</sub></u>	
3099	3110	3105	3100
3085	3090	3085	3080
3085	1417	1410	1402
1408-1411	1385	1380	1378
1356	1178	1178	1175
1178	1170	1152	1142
1105	1022	1020	1020
1010	884	872	865
880	851	850	848
		<u>Class b<sub>1</sub></u>	
3085	3090	3085	3080
3085	3090	3085	3080
1408-1411	1360	1355	1345
1356	1349	1342	1326
(1200)	1205	1202	1200
1178	1153	1152	1150
1010	884	878	883
880	251	237	213
		<u>Class b<sub>2</sub></u>	
1050	1014	1010	1010
834	819	820	820
811	430	410	401
(500)	225	206	180
		<u>Class a<sub>2</sub></u>	
1050	1050	1050	1050
834	805	809	805
(500)	605	599	592

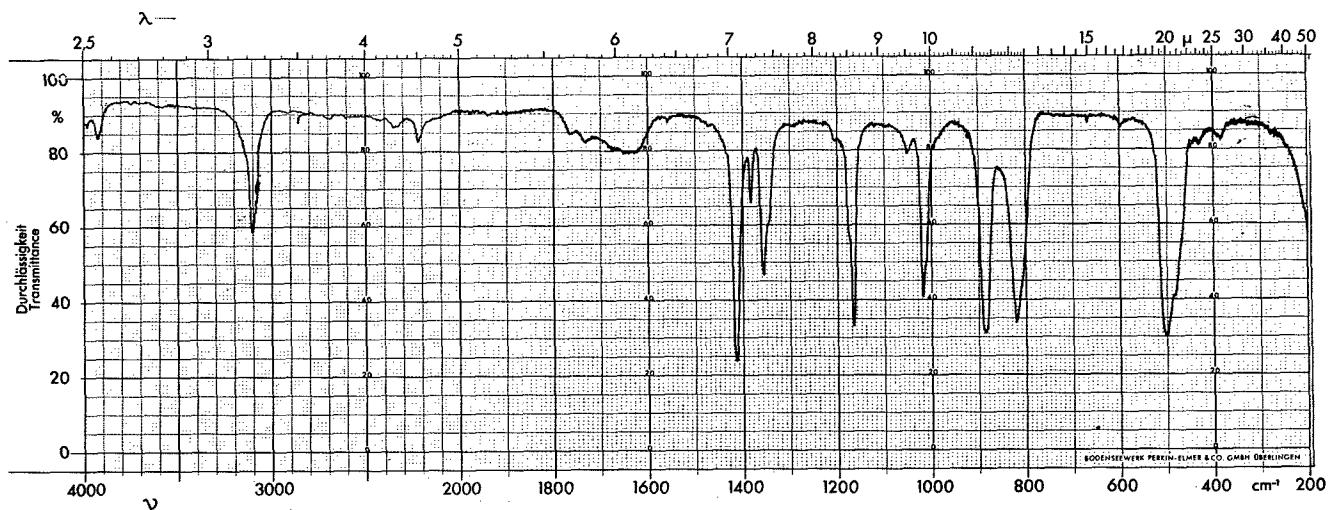


Figure 1. Infrared Spectrum of Liquid Film of 1,1'-Dichloroferrocene

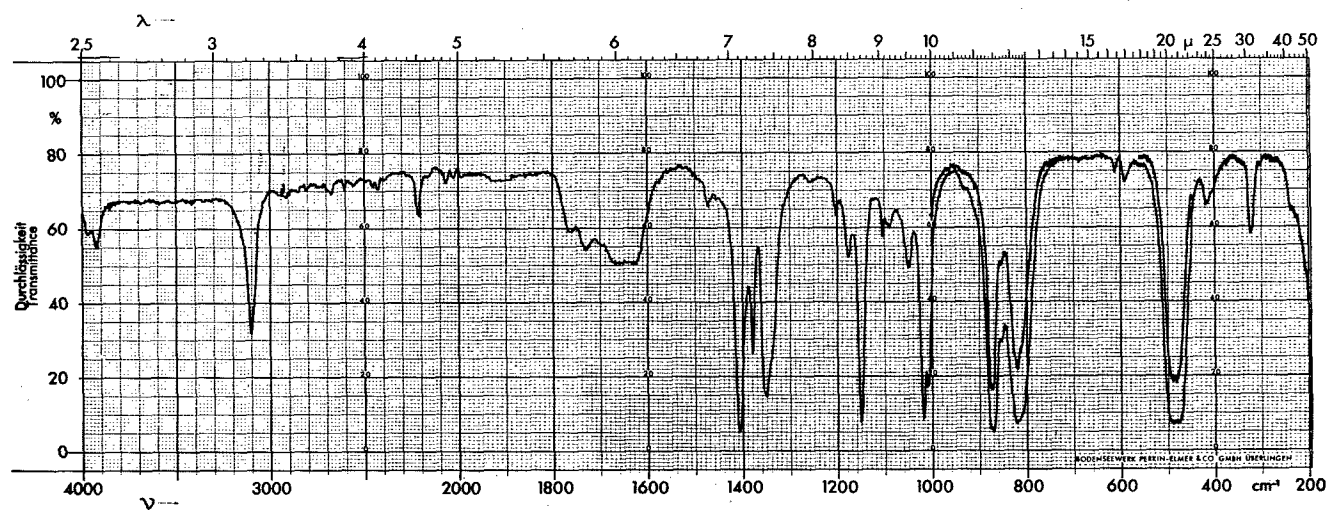


Figure 2. Infrared Spectrum of Liquid Film of 1,1'-Dibromoferrocene

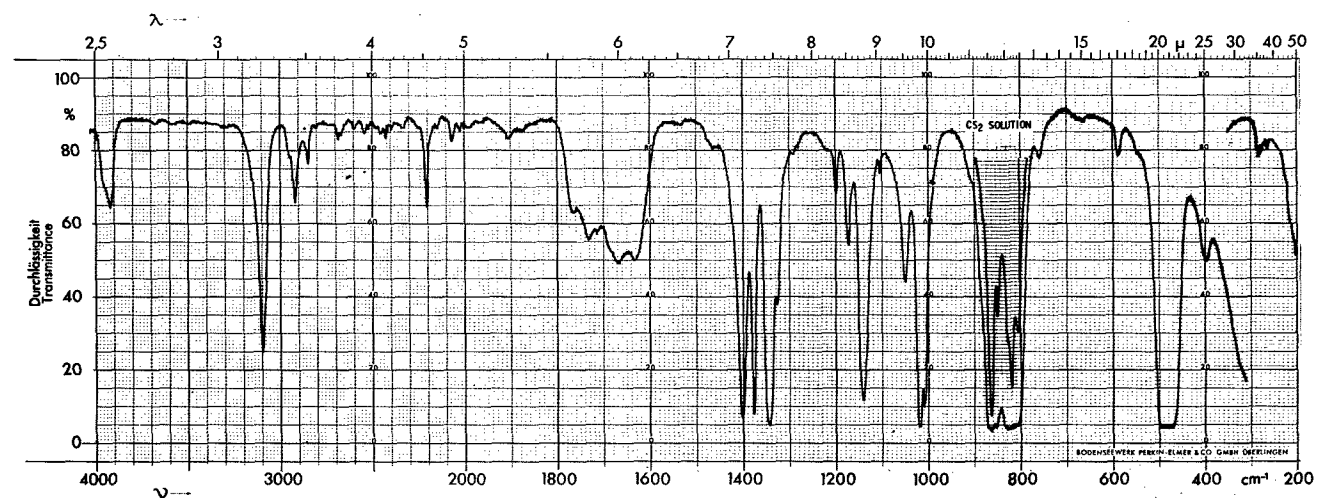


Figure 3. Infrared Spectrum of Liquid Film of 1,1'-Diiodoferrocene

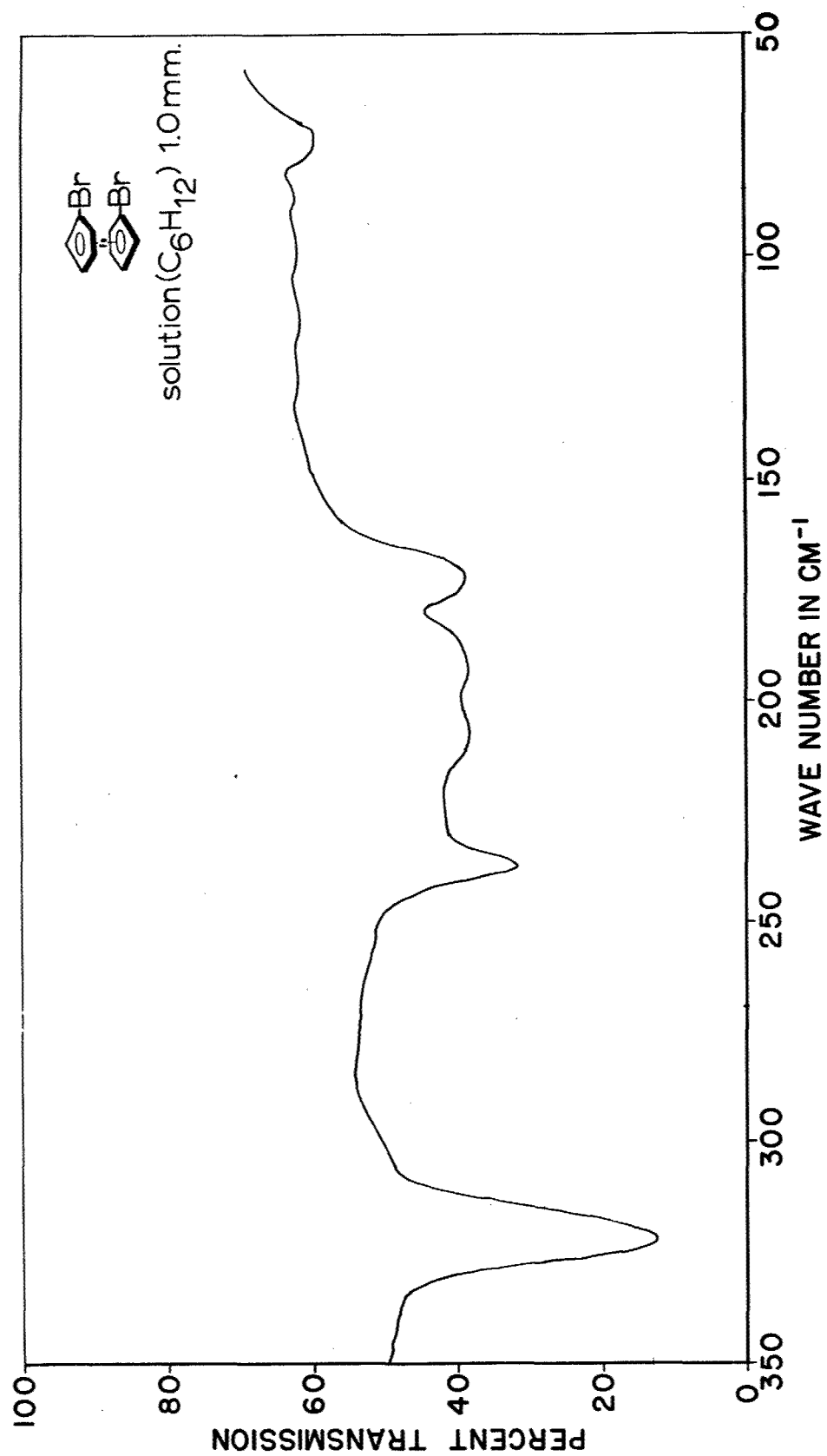


Figure 4. Far Infrared Spectrum of 1,1'-Dibromoferrocene

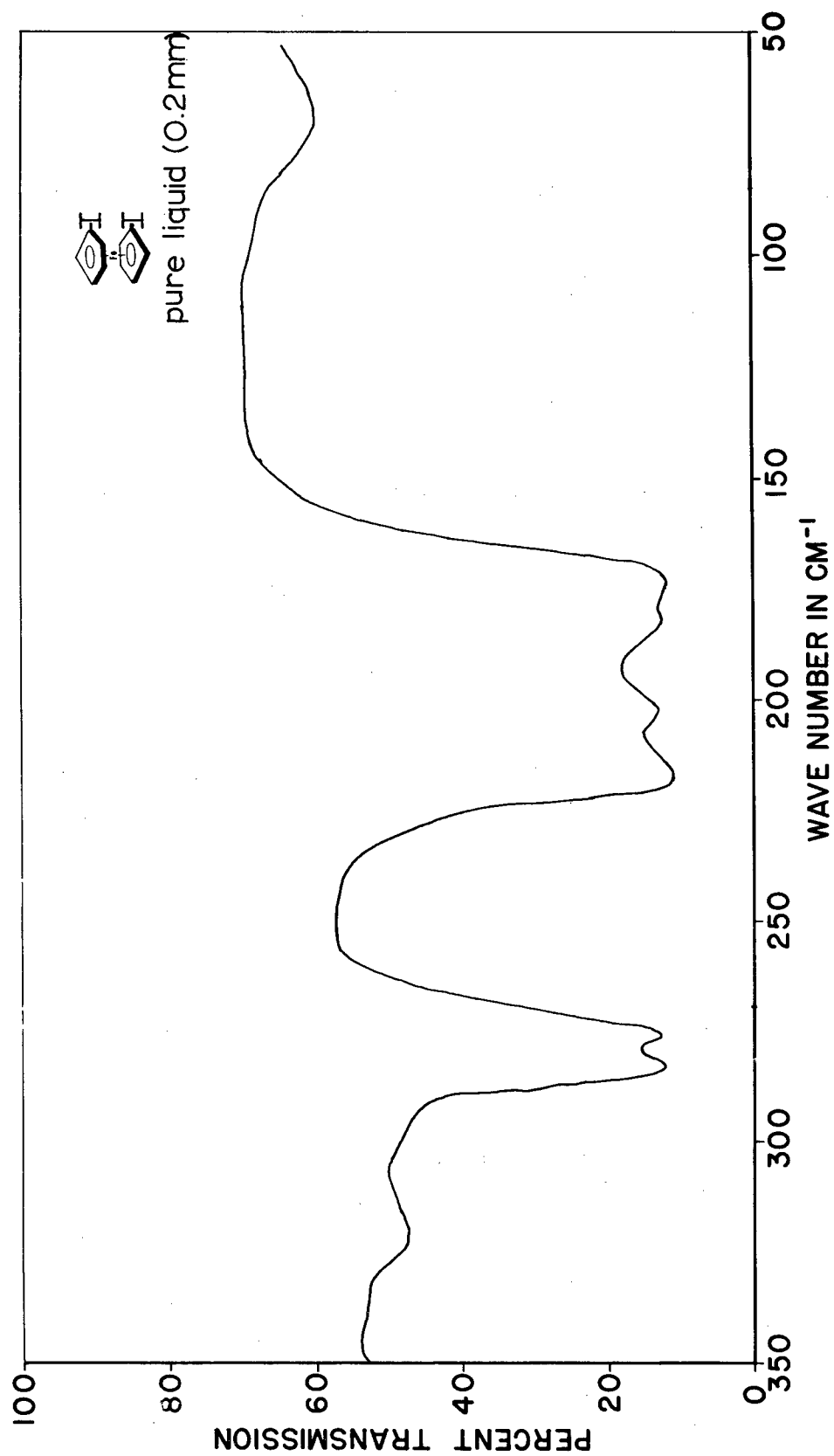


Figure 5. Far Infrared Spectrum of 1, 1'-Diiodoferrocene

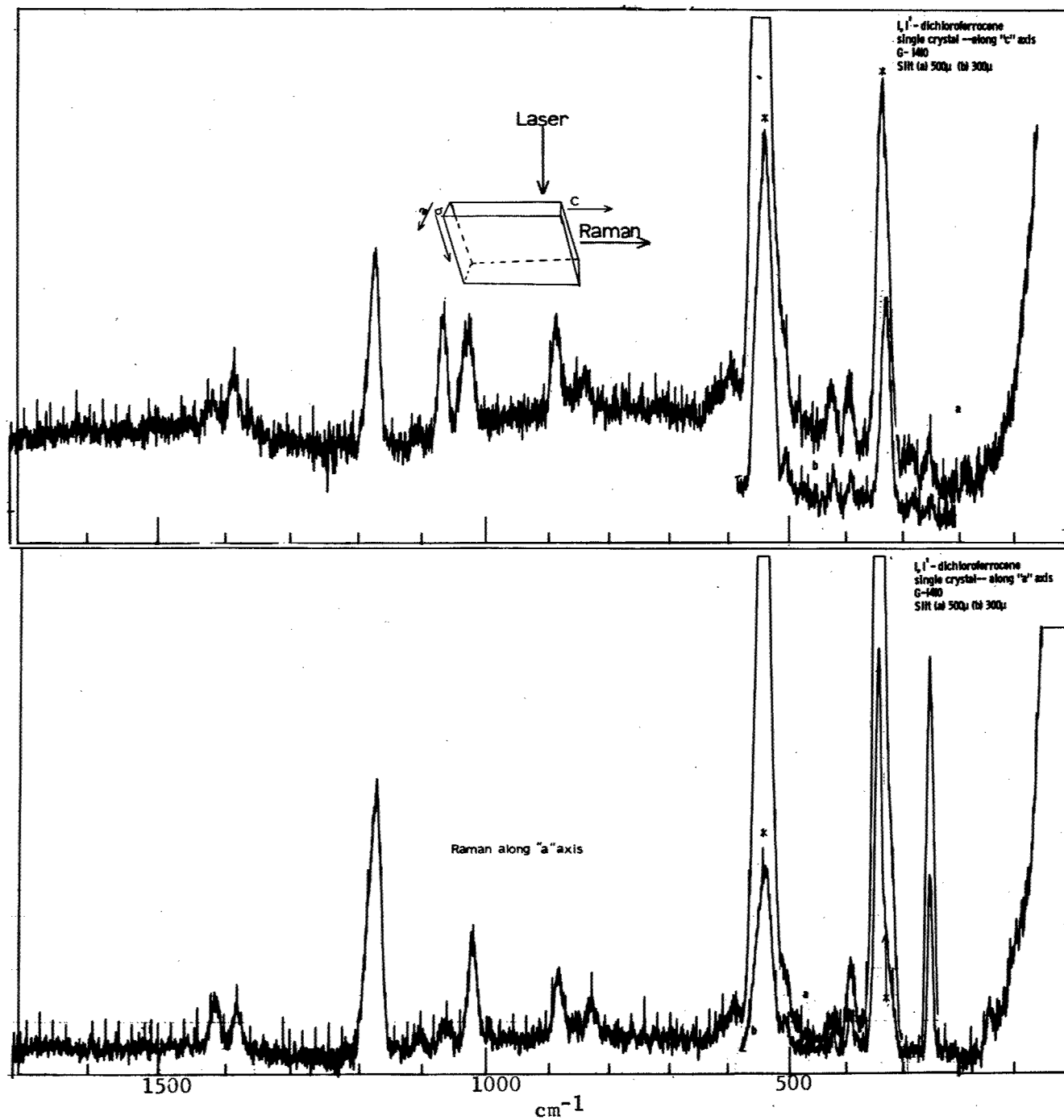


Figure 6. Raman Spectra of Single Crystal 1,1'-Dichloroferrocene

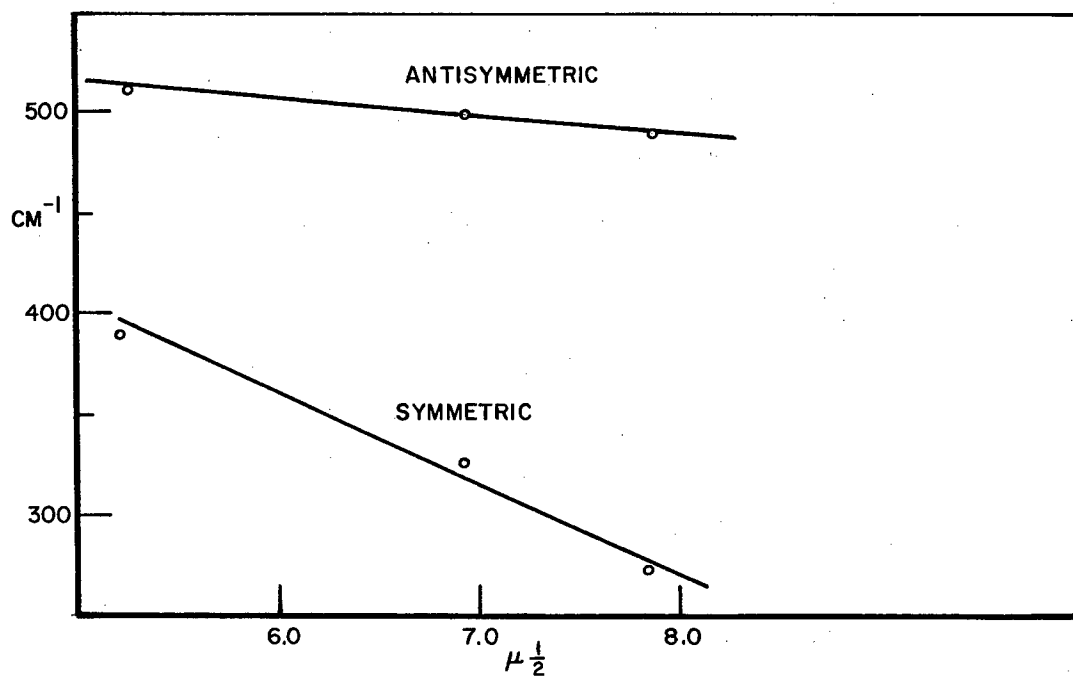


Figure 7. Ring-Metal Tilting Vibration

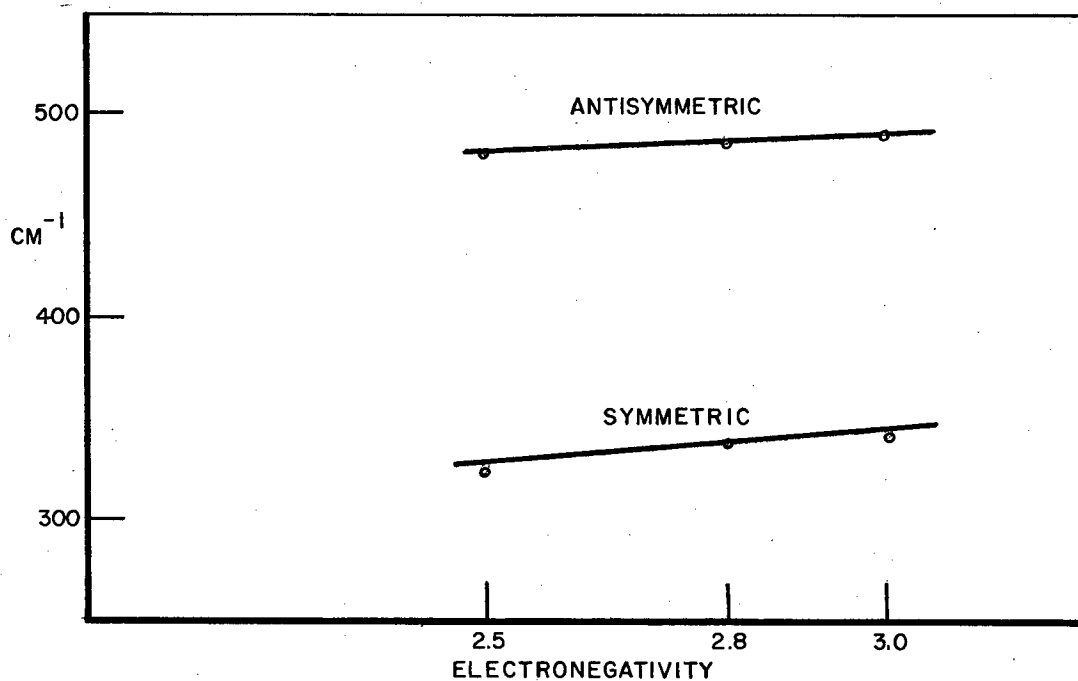


Figure 8. Ring-Metal Stretching Vibration





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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Infrared						
Raman						
Ferrocene						
Vibrational Assignment						

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